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The Oxidation Products of Aluminum Hydride and Boron Aluminum Hydride Clusters

KIT BOWEN
JOHNS HOPKINS UNIV BALTIMORE MD

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"The Oxidation Products of Aluminum Hydride"

Kit Bowen

Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218

Reactions of both Aluminum Hydride Cluster Anions and Boron Aluminum Hydride Cluster Anions with Oxygen: Anionic Products

Abstract

The anionic products of reactions between aluminum hydride cluster anions and oxygen and between boron aluminum hydride cluster anions and oxygen were identified by mass spectrometry. While aluminum oxide anions dominated the products of both reactions, low intensities of hydrogen-containing aluminum oxide product anions were also observed in both cases. Surprisingly, in the reactions between boron aluminum hydride cluster anions and oxygen, there was scant evidence for boron-containing anionic products.

Introduction

Boranes (boron hydrides) were once thought to be promising propellants.¹⁻¹⁴ The reasons derived from their relatively light weight and their high energy release upon oxidation, e.g., $\Delta H^0_{298} = -482.9$ kcal/mol for the reaction, $\text{B}_2\text{H}_6 (\text{g}) + 3\text{O}_2 (\text{g}) \rightarrow \text{B}_2\text{O}_3 (\text{s}) + 3\text{H}_2\text{O} (\text{g})$.¹⁵ The extraordinary exothermicities of borane oxidation reactions are ultimately driven by the high heat of formation of B_2O_3 . Despite their promise, however, the energy actually released by the oxidation of boranes fell well short of expectations. Rather than burning completely to B_2O_3 , the reaction pathway got caught in kinetic traps, whereby hydrogen-, boron-, and oxygen-containing molecules were formed; these effectively blocked the reaction from proceeding to full oxidation. Collectively, these spoiler molecules were known as HOBO compounds.

The “HOBO problem” emerged during the latter half of the 1950’s, during efforts to develop boranes into high performance jet fuels.¹ Ditter and co-workers⁵ reported that the oxidation of pentaborane produced stable hydrogen-, boron-, and oxygen-containing products, among which $\text{H}_2\text{B}_2\text{O}_3$ showed the highest abundance. An additional product, HOBO was 54.8% as prevalent as $\text{H}_2\text{B}_2\text{O}_3$, while B_2O_3 was only 11.1% as prevalent. Bauer *et al.*⁶ also studied the oxidation products of pentaborane, these being found to be HBO, HOBO, and $\text{H}_2\text{B}_2\text{O}_3$. Baden and co-workers⁷ reported that the slow oxidation of pentaborane formed diborane, hydrogen, and a white solid. Whatley *et al.*⁸ studied the products of diborane oxidation. Roth and co-workers⁹ found HOBO to be the main product during the oxidation of diborane. Roth and Bauer¹⁰ proposed that the formation of HOBO severely inhibits the oxidation of boranes by breaking links in its chain reaction mechanism. In summary, boranes never reached their potential as propellants due to the “HOBO problem”.

As boron's sister element, aluminum has been widely utilized in propellants, usually in the form of very small particles.¹⁶⁻²⁰ The best known aluminum hydride analog to the boranes is alane (AlH_3). Unlike boranes, which tend to be gases, alane is a solid with six crystalline phases. In principle, alane is a promising propellant. The specific impulse of an AP/HTPB propellant mixed with alane was calculated to be 100 N s kg^{-1} higher than the same propellant mixed with the same concentration of aluminum.²¹ Furthermore, the flame temperature of alane-containing propellants was 15% lower than that of aluminum-containing propellants, resulting in a lower need for thermal protection of the rocket.²² The mechanism of alane combustion was proposed to be: $\text{AlH}_3 \rightarrow \text{Al} + 3/2 \text{ H}_2$ (dehydrogenation), followed by $\text{Al} + 3/4 \text{ O}_2 \rightarrow 1/2 \text{ Al}_2\text{O}_3$ (oxidation).²³ Both the hydrogen release temperature and the ignition temperature were lower than aluminum's melting point.²² Despite these advantages, however, alane has seen relatively little use as an ingredient in propellants. Its Achilles heel appears to be its poor thermal stability, although materials purity issues may have also contributed to its lack of acceptance as a propellant.^{22,24}

While alane is the only aluminum hydride to have been studied in macroscopic quantities, aluminum hydride cluster anions, Al_yH_z^- , have been prepared and extensively characterized in molecular beam environments. Al_4H_6 cluster was reported to have exceptional stability, and its heat of combustion was calculated to be 438 kcal/mol , i.e., ~ 2.6 times greater than that of methane.²⁵ Subsequent studies discovered and characterized *hundreds* of previously unknown aluminum hydride cluster anions, Al_yH_z^- .²⁶⁻³² Additionally, about 80 *boron* aluminum hydride cluster anions, $\text{B}_x\text{Al}_y\text{H}_z^-$, have also been discovered and characterized.³³

The availability of aluminum hydride cluster anion beams makes it possible to determine whether the products of reactions between Al_yH_z^- and O_2 exhibit a "HOAIO problem". Likewise, the availability of boron aluminum hydride cluster anion beams makes it possible to determine

whether the products of reactions between $B_xAl_yH_z^-$ and O_2 exhibit a “HOAlO problem”, a “HOBO problem”, or both. Intuition suggests that reactions between $Al_yH_z^-$ and O_2 will go to complete oxidation, avoiding a hypothetical “HOAlO problem”. Given this expectation and the history of HOBO formation in reactions between boranes and O_2 , it is interesting to consider whether the presence of aluminum in $B_xAl_yH_z^-$ might carry its boron moiety along with it to complete oxidation during reactions between $B_xAl_yH_z^-$ and O_2 , or whether the formation of HOBO-like products will continue to prove resilient. Can reactions between $B_xAl_yH_z^-$ and O_2 bypass the “HOBO problem”?

In the present work, we determine the identities of the anionic products of reactions between $Al_yH_z^-$ and O_2 and between $B_xAl_yH_z^-$ and O_2 . This is accomplished by directing cluster anion beams through a low-density reaction cell containing O_2 , after which the emerging anionic products are identified by mass spectrometry. This methodology allows us to detect and identify the anionic forms of any HOAlO and/or HOBO products formed by these reactions. Previous studies of borane oxidation used mass spectrometry to identify the cations of neutral HOBO products. Here, our use of mass spectrometry to identify the anionic products of $Al_yH_z^-$ and $B_xAl_yH_z^-$ oxidation reactions is potentially a more sensitive method of detecting HOAlO and HOBO molecules, given that aluminum and boron compounds tend to be electrophilic and thus to readily form negative ions.

Experimental and Computational Methods

Both aluminum hydride and boron aluminum hydride cluster anions, $Al_yH_z^-$ and $B_xAl_yH_z^-$, were generated in a pulsed arc cluster ionization source (PACIS), which has proven to be a powerful tool for generating metal and metal hydride cluster anions.^{25,33-44} Briefly, a $\sim 30\ \mu s$

duration, 150 V electrical pulse applied across the anode and the sample cathode vaporizes the sample atoms and forms a plasma. In the present case, the sample cathode is a 0.5 inch diameter pure aluminum rod or alternatively a boron/aluminum powder mixture which had been firmly pressed onto a shallow cup in the top of the aluminum rod. About 200 psi of ultrahigh purity hydrogen gas was then injected through a pulsed valve into the arc region, where it was dissociated into hydrogen atoms, before the resulting plasma/gas mixture was propelled down a 3 cm diameter tube. Cluster anions generated in this way then drifted through a gap before entering the 10 cm long, 1 cm diameter reaction cell with 2 mm diameter apertures on both ends. Next, ~50 psi of oxygen was injected into the cell by another pulsed valve located on the side of the reaction cell. The two end-apertures helped to contain the oxygen and to limit any back flow. With no oxygen in the cell, Al_yH_z^- or $\text{B}_x\text{Al}_y\text{H}_z^-$ species continued on into the extraction grids of a time-of-flight mass spectrometer, where they were identified, but when oxygen was added to the cell and anionic reaction products were formed, they too were identified by mass spectrometry.

In the cases of the anionic HOAlO products, it was also of interest to characterize their geometries. Density functional theory calculations were conducted by applying Becke's three-parameter hybrid functional (B3LYP)⁴⁵⁻⁴⁷ using the Gaussian09 software package⁴⁸ to determine the geometries of anionic H_2AlO_4^- and HAl_2O_4^- . All geometries were fully optimized using the 6-311++G (3df, 3pd) basis set.

Results

Figure 1(a) shows a typical mass spectrum of Al_yH_z^- ($y = 2 - 7$), produced by the PACIS source. Figure 1(b) presents the same mass spectral range, once O_2 has been introduced into the reaction cell. While many different anionic products appeared in Figure 1(b), including AlO^- ,

AlO_2^- , $\text{H}_{0.2}\text{AlO}_3^-$, $\text{H}_{0.1}\text{Al}_2\text{O}_2^-$, H_2AlO_4^- , $\text{H}_{0.1}\text{Al}_2\text{O}_3^-$, $\text{H}_{0.1}\text{Al}_2\text{O}_4^-$, Al_3O_3^- , Al_2O_5^- , and Al_3O_5^- , the most intense among them was Al_3O_3^- . Setting the intensity of Al_3O_3^- at 100%, the relative intensities of the other anionic products are listed in Table 1. The most abundant HOAlO-type products are H_2AlO_4^- and HAl_2O_4^- , these being 19% and 12% of the intensity of Al_3O_3^- , respectively. Additional HOAlO-type anionic products were HAl_2O_2^- , HAl_2O_3^- , H_2AlO_3^- , and HAlO_3^- , although their intensities are weaker. Both of these “before” and “after” mass spectra have been repeated many times in close sequence. Furthermore, the product anion relative intensities reported in Table 1 were relatively constant from run to run. The unmarked mass peaks in Figure 1(b) are likely due to unreacted aluminum hydride cluster anions, all of which exhibit very low intensities. It is clear, however, that most aluminum hydride cluster anions had burned.

Figure 2(a) shows a typical mass spectrum of $\text{B}_x\text{Al}_y\text{H}_z^-$ ($x = 2, 3$), these species having also been generated in the PACIS source. While Al_yH_z^- species are present there, the $\text{B}_x\text{Al}_y\text{H}_z^-$ ($x = 2, 3$) species clearly dominate. Figure 2(b) presents the same mass spectrum, once O_2 has been introduced into the reaction cell. The anions appearing in Figure 2(b) included BO_2^- , AlO^- , AlO_2^- , AlO_3^- , H_2AlO_4^- , Al_2O_3^- , $\text{H}_{0.1}\text{Al}_2\text{O}_4^-$, Al_3O_3^- , Al_2O_5^- , Al_3O_4^- , and Al_3O_5^- , with Al_3O_3^- again exhibiting the highest intensity. Many of the species seen in Figure 1(b) are also present in Figure 2(b). Setting the intensity of Al_3O_3^- at 100%, the relative intensities of the other anionic products in Figure 2(b) are listed in Table 2. Like the mass spectra of Figures 1(a) and 1(b), the mass spectra of Figures 2(a) and 2(b) have been repeated many times in close sequence. Again, the product anion relative intensities reported in Table 2 were relatively constant from run to run. Unmarked mass peaks in Figure 2(b) may well be unreacted cluster anions of the types seen in Figure 2(a).

Mass coincidences significantly complicate the delineation between boron-containing and aluminum-containing species, e.g., the masses of ^{11}BO and of Al are the same. Nevertheless, the presence of ^{10}B , which is 24.7% as abundant as ^{11}B , helps to sort out some mass coincidences. For example, while the masses of AlO^- and $^{11}\text{BO}_2^-$ are the same (43 amu), the appearance in Figure 2(b) of a mass peak at 42 amu, i.e., $^{10}\text{BO}_2^-$, strongly suggests that BO_2^- is present [see inset in Figure 2(b)]. On the other hand, the mass of AlO_2^- is the same as that of $^{11}\text{BO}_3^-$ (59 amu), but since there is no significant intensity at 58 amu, it is clear that BO_3^- is not present in the mass spectrum.

There are two types of boron-containing species that might reasonably be expected to appear in Figure 2(b) in addition to aluminum oxide anions, HOAlO-type anions, and unreacted $\text{B}_2\text{Al}_y\text{H}_z^-$, $\text{B}_3\text{Al}_y\text{H}_z^-$, and Al_yH_z^- species. These are boron oxide anions and HOB O-type anions. Numerous prominent aluminum oxide anion peaks do indeed appear in Figure 2(b). Focusing on the stoichiometries of those aluminum oxide anions as guides, we examined the mass spectrum in Figure 2(b), looking for the presence of boron oxide anion analogs to Al_3O_3^- , Al_2O_5^- , Al_3O_5^- , Al_2O_3^- , AlO_2^- , Al_2O_4^- , Al_3O_4^- , and AlO_3^- . The most intense mass spectral aluminum oxide anion peak is that of Al_3O_3^- . Its boron counterpart, B_3O_3^- , should appear over the mass range, 78-81 amu. Upon magnifying the mass spectrum in Figure 2(b), we saw only weak intensity peaks in this mass range, and these also exhibited the wrong isotope pattern. Moreover, upon magnifying Figure 2(a), we also saw mass peaks of unreacted species at these same masses. Except for BO_2^- , the same conclusions were reached for B_2O_5^- , B_3O_5^- , B_2O_3^- , BO_2^- , B_2O_4^- , B_3O_4^- , and BO_3^- . They were either absent or mistaken for unreacted species: again, see Figure 2(a). Even if some of them did occur in the mass spectrum, it is clear that their intensities were quite weak.

We also searched the magnified mass spectrum of Figure 2(b), looking for HOBO-type anions. Again, we took our clue from the stoichiometries of HOAlO-type anions that are present in Figure 2(b), i.e., H_2AlO_4^- and HAl_2O_4^- . The mass positions of both H_2BO_4^- (76 & 77 amu) and HB_2O_4^- (85 – 87 amu) show peaks with enticing isotope patterns, but their intensities are weak, and at best they may be entangled with peaks from unreacted species; *cf.*, Figure 2(a). For both boron oxide anions and HOBO-type anions in Figure 2(b), most of them were either absent or present only at low intensities, where even those may have been obscured by unreacted anions as seen in Figure 2(a). Surprisingly, there is little evidence of boron-containing anionic species in Figure 2(b).

Discussion

The majority of the anionic products observed due to the oxidation of aluminum hydride and boron aluminum hydride anions were aluminum oxide (cluster) anions. In some of these, e.g., AlO_2^- and Al_3O_5^- , aluminum is in its highest oxidation state. However, in its most abundant product, Al_3O_3^- , it is not. The Al_3O_3^- ion can be viewed as $(\text{Al}_3)^{5+}(\text{O}^{2-})_3^-$,⁴⁹ and its unusual stability can be attributed to its six member ring structure. Also, while Al_2O_3 , with its Al(+3) oxidation state, would be expected to be the favored (most stable) neutral product in aluminum compound oxidation reactions, the Al_2O_3^- anion, with its additional electron and thus its lower Al oxidation state, is not.⁵⁰

While aluminum oxide anions were clearly the dominate reaction products of the oxidation of both aluminum hydride and boron aluminum hydride anions, low intensities of HOAlO product anions were also observed in both cases. The hydrogen-containing, aluminum oxide product anions, H_2AlO_4^- and HAl_2O_4^- are representative. Their calculated structures are presented in Figure 3, where all bond lengths are given in Angstroms, Å. H_2AlO_4^- has a

tetrahedral structure, where two hydroxyl groups and a peroxide moiety are attached to the central aluminum atom. Its vertical detachment energy was calculated to be 3.73 eV. HAl_2O_4^- is planar, with the two aluminum atoms connected through two bridging oxygen atoms and with one oxygen atom and one hydroxyl group forming radial bonds with the two aluminum atoms. Its vertical detachment energy was calculated to be 3.78 eV. Thus, contrary to conventional wisdom, the oxidation of aluminum hydride (cluster) anions does have a “HOBOf-like problem”, i.e., the appearance of HOAlO-type anion products, although it is quite minor compared to the dominant HOBOf-type products observed due to the oxidation of boranes.

Despite our experiments being repeated many times, we observed little evidence for the presence of boron in the mass spectrum presented in Figure 2(b). Specifically, other than BO_2^- , we saw no definitive evidence for other boron oxide anions or for HOBOf-type anions in Figure 2(b). Where is the boron? This is admittedly a paradox. Perhaps, boron-containing anionic species are hidden by mass coincidences or buried under the mass peaks of unreacted species. It seems more likely that the boron-containing molecules are present as neutral products. During long boron aluminum hydride runs, the downstream window became thinly coated with a brown film, suggesting the deposition of neutral products. With the same exposure time, this does not happen during aluminum hydride runs. Still, the “boron dark matter” dilemma remains unsatisfactorily explained; it will be the subject of future experiments in our lab.

When we began these anion reactivity studies, we hypothesized that the oxidation of aluminum hydride (cluster) anions would not exhibit a HOBOf-like problem, i.e., a HOAlO-type problem, focusing our attention on whether the oxidation of boron aluminum hydride anions might bypass the “HOBOf problem”. We learned instead that the oxidation of aluminum hydride (cluster) anions does in fact exhibit a “HOBOf-type problem”, although only mildly compared to

that seen in the oxidation of boranes. The idea of using boron aluminum hydrides to minimize or even eliminate the “HOBO problem” also dealt us surprises. While we did not see evidence of HOBO-like anionic species, we also could not account for the disposition of boron generally, e.g., as boron oxide anions.

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Table 1. The relative intensities of the major anionic products due to reactions between aluminum cluster anions and oxygen. The intensity of Al_3O_3^- is set to be 100%.

| Species | Mass (amu) | Relative Intensity (%) |
|----------------------------|------------|------------------------|
| Al_3O_3^- | 129 | 100.0 |
| AlO_2^- | 59 | 43.9 |
| H_2AlO_4^- | 93 | 19.0 |
| Al_2O_5^- | 134 | 17.9 |
| Al_2O_3^- | 102 | 13.1 |
| HAl_2O_4^- | 119 | 12.3 |
| Al_3O_5^- | 161 | 9.2 |
| HAl_2O_2^- | 87 | 6.4 |
| Al_2O_2^- | 86 | 5.0 |
| HAl_2O_3^- | 103 | 4.8 |
| H_2AlO_3^- | 77 | 3.9 |
| Al_2O_4^- | 118 | 3.6 |
| AlO_3^- | 75 | 2.2 |
| HAlO_3^- | 76 | 2.0 |
| AlO^- | 43 | 1.1 |

Table 2. The relative intensities of the major anionic products due to reactions between boron aluminum cluster anions and oxygen. The intensity of Al_3O_3^- is set to be 100%.

| Species | Mass (amu) | Relative Intensity (%) |
|----------------------------|------------|------------------------|
| Al_3O_3^- | 129 | 100.0 |
| Al_2O_5^- | 134 | 58.2 |
| AlO_2^- | 59 | 56.4 |
| Al_3O_5^- | 161 | 28.4 |
| Al_2O_3^- | 102 | 26.1 |
| HAl_2O_4^- | 119 | 14.4 |
| AlO_3^- | 75 | 13.8 |
| Al_2O_4^- | 118 | 13.7 |
| Al_3O_4^- | 145 | 13.3 |
| H_2AlO_4^- | 93 | 10.2 |
| AlO^- | 43 | 3.2 |
| BO_2^- | 42 and 43 | 2.9 |

Figure Captions

Figure 1. Typical mass spectra of Al_yH_z^- : (a) before the addition of O_2 into the reaction cell and (b) after the addition of O_2 into the reaction cell, i.e., the anionic reaction products.

Figure 2. Typical mass spectra of $\text{B}_x\text{Al}_y\text{H}_z^-$ and Al_yH_z^- : (a) before the addition of O_2 into the reaction cell and (b) after the addition of O_2 into the reaction cell, i.e., the anionic reaction products. The embedded mass spectrum in Figure 2(b) shows the presence of BO_2^- along with AlO^- .

Figure 3. Calculated structures of H_2AlO_4^- and HAl_2O_4^- . All the bond lengths are in Å.

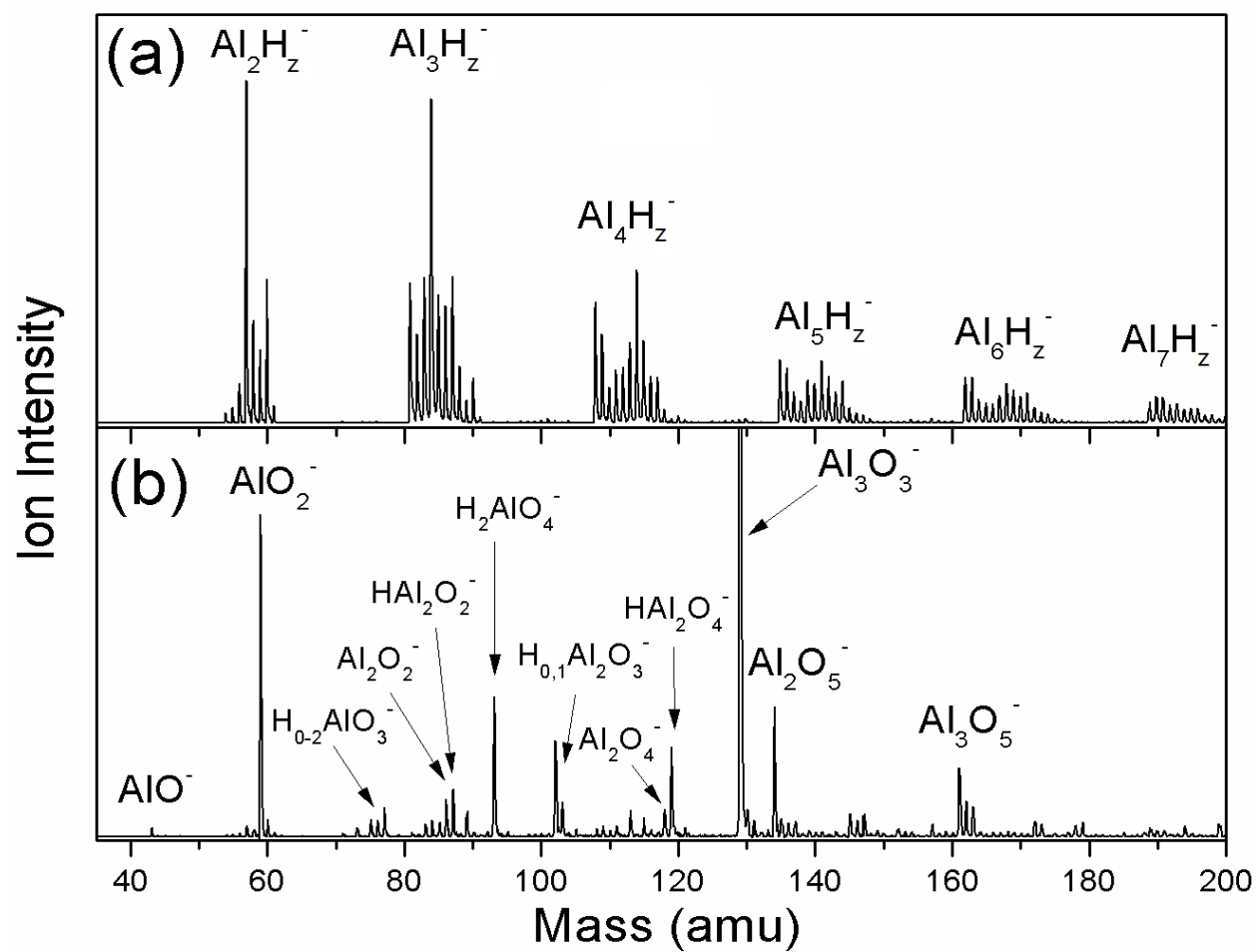


Figure 1

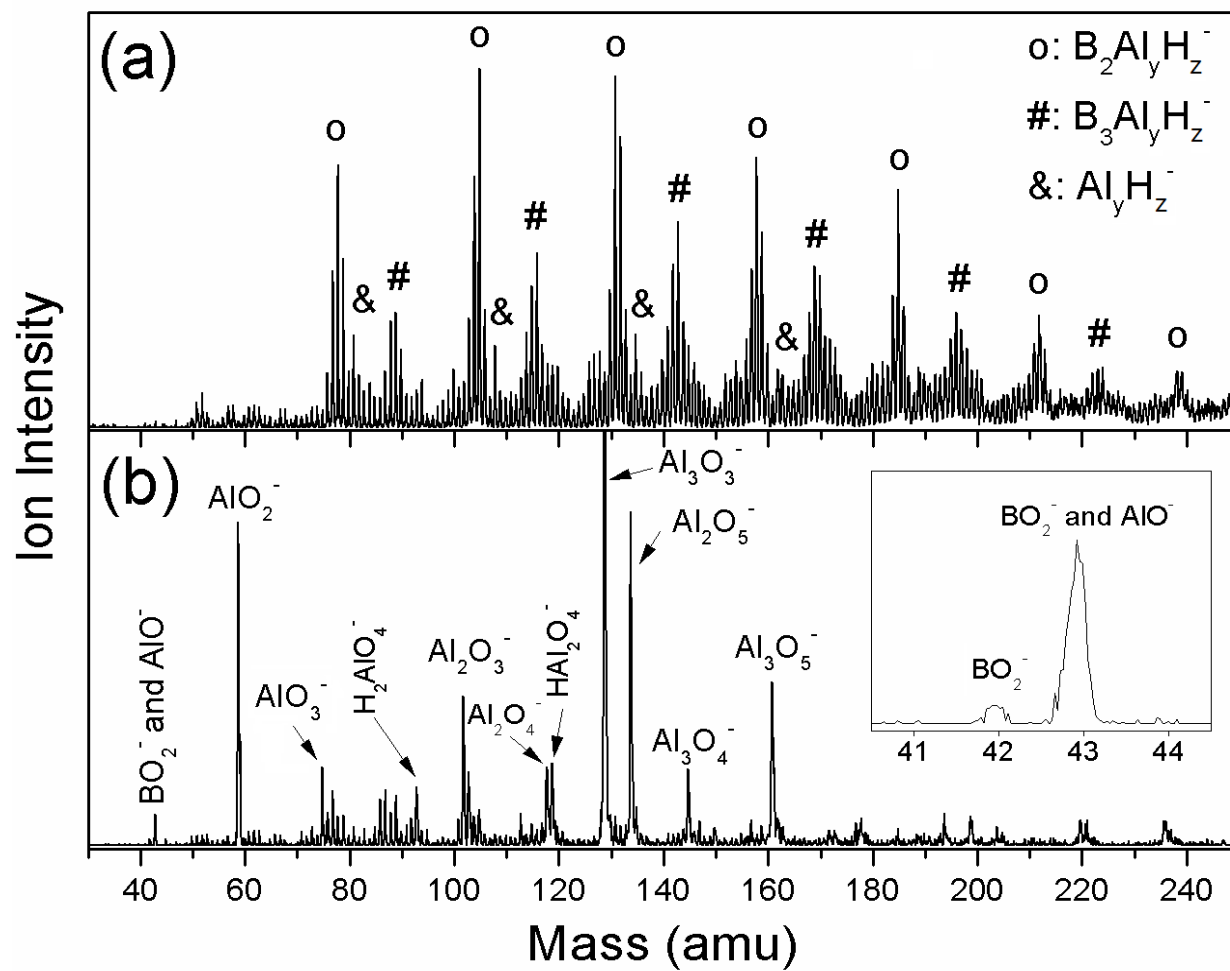


Figure 2

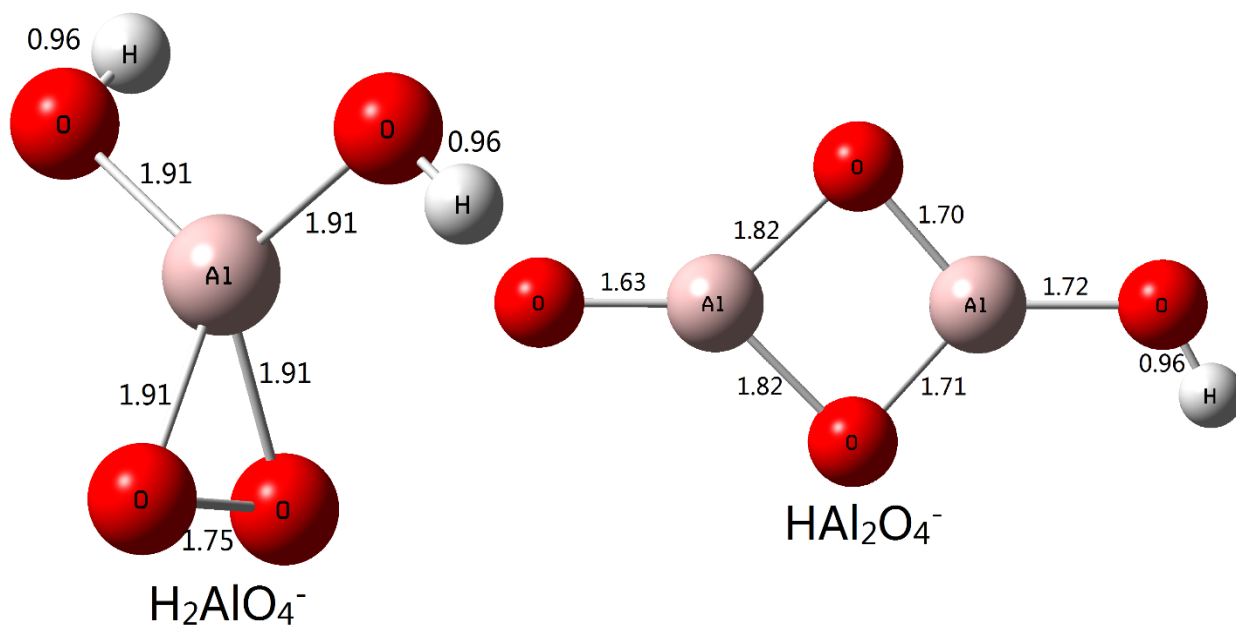


Figure 3

1.

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The Oxidation Products of Aluminum Hydride

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FA9550-14-1-0324

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

Kit Bowen

Program Manager**The AFOSR Program Manager currently assigned to the award**

Dr. Michael Berman

Reporting Period Start Date

09/30/2014

Reporting Period End Date

09/29/2015

Abstract

Reactions of both Aluminum Hydride Cluster Anions and Boron Aluminum Hydride Cluster Anions with Oxygen: Anionic Products

The anionic products of reactions between aluminum hydride cluster anions and oxygen and between boron aluminum hydride cluster anions and oxygen were identified by mass spectrometry. While aluminum oxide anions dominated the products of both reactions, low intensities of hydrogen-containing aluminum oxide product anions were also observed in both cases. Surprisingly, in the reactions between boron aluminum hydride cluster anions and oxygen, there was scant evidence for boron-containing anionic products.

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Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

No

Extensions granted or milestones slipped, if any:

None

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

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Appendix Documents

2. Thank You

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